

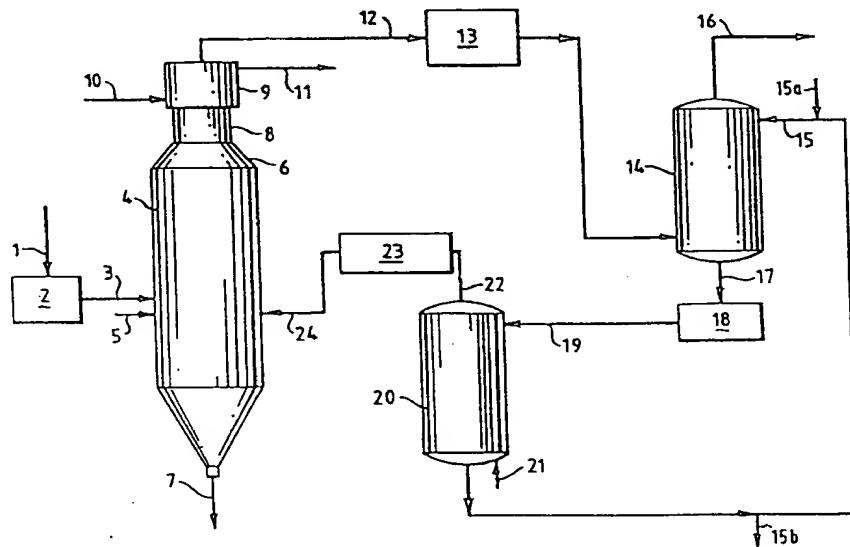
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(54) Removal of HCN, NH₃ and COS from synthesis gas

(57) A process for the gasification of coal or other carbonaceous matter is disclosed, the process being characterized by scrubbing of HCN, NH₃ and COS from the synthesis gas stream with an aqueous solution at 14, stripping of the aqueous solution to release the HCN, NH₃ and COS at 20, and consumption of the HCN, NH₃ and COS in the gasification step at 4. The gas stream may be cooled prior to scrubbing. Particulate matter may be removed from the gas stream before or during scrubbing.



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SPECIFICATION

Removal of HCN, NH₃ and COS from synthesis gas

5 The invention relates to a process for the gasification of carbon-containing fuel.

Partial combustion or gasification of a carbonaceous material, such as coal, involves reacting the material at elevated temperatures with a limited volume of oxygen, the reaction advantageously being carried out in the presence of additional agents such as steam, carbon dioxide, or various other materials. Gasification produces a gas, known as synthesis gas, that contains mostly carbon monoxide and hydrogen. Also produced are varying quantities of other gases, such as carbon dioxide and methane, and various liquid and solid materials, such as small particles of ash. In general, the solid materials entrained with the gas are usually removed from the raw synthesis gas by a combination of cyclones or separators, or a water scrubbing system employing washer coolers, venturi scrubbers, or filters or electrostatic precipitators, or combinations of these systems.

25 The raw synthesis gas from the gasifier or gasification zone contains, in addition to the aforementioned materials, sulphur-containing gases, such as hydrogen sulphide and carbonyl sulphide, as well as small amounts of ammonia and hydrogen cyanide.

30 The presence of HCN, NH₃ and COS (carbonyl sulphide) in synthesis gas derived from the gasification of a carbon-containing fuel such as coal complicates removal of additional impurities such as H₂S and/or CO₂, and poses problems insofar as product quality 35 and pollution control requirements are concerned. Although HCN, NH₃ and COS are present, as indicated, in quite minor quantities, for example, normally less than 1 per cent by volume, combined, of the total raw synthesis gas stream, they must be dealt with 40 before the synthesis gas is utilized.

Accordingly, a practical and efficient procedure for removing these impurities might have great economic importance. It is therefore an object of the invention to provide a process for the gasification of a 45 carbonaceous material wherein these impurities are removed in a practical and efficient manner.

The invention, therefore relates to a process for the gasification of carbon-containing fuel comprising the steps of

50 (a) partially combusting particulate carbon-containing fuel in a gasification zone comprising at least one gasification reactor, and producing a gaseous stream containing synthesis gas, particulate matter, and minor amounts of HCN, NH₃ and COS;

55 (b) cooling said gaseous stream, and removing at least the bulk of the particulate matter therefrom, and scrubbing said gaseous stream in a scrubbing zone with an effective amount of an aqueous scrubbing solution and removing HCN, NH₃, COS and remaining particulate matter from said synthesis gas, producing a purified synthesis gas and loaded scrubbing solution;

(c) stripping the bulk of the HCN, NH₃ and COS from at least a portion of said loaded scrubbing solution in a stripping zone, producing a gas mixture

containing HCN, NH₃ and COS, and a stripped liquid mixture, and removing said gas mixture from said stripped liquid mixture and said stripping zone; and

70 (d) introducing at least a portion of said gas mixture into at least one gasification reactor of said gasification zone.

Upon introduction of the gas mixture into the gasification zone, the afore-mentioned impurities are converted substantially to disposable and/or usable

75 gaseous materials. In an advantageous embodiment of the invention at least the bulk of the stripped liquid mixture is sent to the scrubbing zone for use therein as the aqueous scrubbing mixture. Further, particulate matter may be separated from the aqueous 80 admixture prior to its entry into the stripping zone, or particulate matter may be separated from the stripped liquid mixture prior to being introduced into the scrubbing zone.

The partial combustion of carbon-containing materials, for example, coal, to produce synthesis gas, which is essentially carbon monoxide and hydrogen, is well known, and a survey of known processes is given in "Ullmanns Enzyklopädie Der Technischen Chemie", vol. 10 (1958), p. 360-458. Several such processes for the preparation of hydrogen and carbon monoxide-containing gases are currently being developed. Accordingly, details of the gasification process are related only insofar as is necessary for understanding of the present invention.

90 95 In general, the gasification of the carbonaceous material is carried out by partially combusting the material with a limited volume of oxygen at a temperature normally between 800°C and 2000°C, and advantageously at a temperature between 1050°C and 2000°C. If a temperature of between 1050°C and 2000°C is employed, the product gas may contain very small amounts of gaseous side products such as tars, phenols and condensable hydrocarbons. The carbon-containing starting materials may include

100 105 lignite, bituminous coal, sub-bituminous coal, anthracite coal, coke, wood, and heavy petroleum residues. Lignites and coals are advantageous carbonaceous materials. In order to achieve a more rapid and complete gasification, initial pulverization of

110 115 solid carbon-containing starting materials is advantageous. Particle size of this material can be selected so that 70% of the solid feed can pass a 200 mesh sieve. The gasification is advantageously carried out in the presence of oxygen and steam, the purity of the

120 125 oxygen advantageously being at least 90% by volume, nitrogen, carbon dioxide and argon being permissible as impurities. Although, in general, the ratio between oxygen and steam can be selected so that from 5 to 60 parts by volume of steam is present per part by volume of oxygen, the invention is applicable to processes having substantially different ratios of oxygens to steam. The oxygen used can be heated before being contacted with the carbon-containing material, for example to a temperature of from about 200°C to about 500°C.

The details of the gasification reactor system form no part of the present invention, and suitable reactors are described in British Patent Specification No. 0601284 and US Patent Specification No. 4,022,591.

130 The high temperature at which the gasification is car-

ried out is obtained by reacting the carbonaceous material with oxygen and steam in a reactor at high velocity. An advantageous linear velocity is from 10 to 100 metres per second, although higher or lower velocities may be employed. The pressure at which the gasification can be effected may vary between wide limits, for example from 1 to 200 bar. Residence times may vary widely; common residence times of from 0.2 to 20 seconds are described, with residence times of from 0.5 to 15 seconds being advantageous.

After the starting materials have been converted, the reaction product, which comprises hydrogen, carbon monoxide, carbon dioxide, and water, as well as the afore-mentioned impurities, is removed from the reactor. This gas, which normally has a temperature between 1050°C and 1800°C, may contain impurities such as ash and carbon-containing solids. In order to permit removal of the impurities from the gas, the reaction product stream should first be cooled. A variety of elaborate techniques have been developed for cooling the gaseous stream, the techniques in general being characterized by use of a boiler in which steam is generated with the aid of the waste heat. Cyclones or other suitable techniques may be provided for removing particulate solids from the gaseous stream. Even though such procedures may be practised, further reduction of the solids content may nevertheless be desirable. To this end, the gas stream can be passed through a scrubbing zone, where it is washed with an aqueous scrubbing solution. The scrubbing zone may comprise one or more scrubbing sections or "scrubbers". The term "aqueous scrubbing solution", as used herein, includes, but is not limited to, water, various process streams, and solution from which the HCN, NH₃ and COS have been stripped, i.e., recycle. The aqueous scrubbing solution may contain materials, such as selective amines, to assist in impurity removal, and caustic may be added to adjust pH and optimize removal. Water can be applied for HCN and NH₃, and amine solution may be added for COS removal, in a separate stage, if desired. If more than one stage is employed, the solutions may or may not be combined before their entry into the stripping zone.

Those skilled in the art may adjust the pH, composition, and volumes of aqueous scrubbing solution to supply an amount effective to remove substantially all, if not all, of the HCN, NH₃ and COS from the synthesis gas stream. Suitable scrubbing apparatus has been described in UK Patent Specification No. 826,209. As a result of such a washing treatment, a gas is obtained which contains hardly any solids, and which has a temperature between 20°C and 40°C.

As indicated, in addition to removing particulates remaining in the gaseous stream, the aqueous scrubbing solution will also remove quantities of HCN, ammonia and COS. The invention focuses on the treatment of the contaminated or "loaded" scrubbing solution, with the aim of substantially reducing the output of HCN, NH₃ and COS to be treated or disposed of. As used herein, the term "loaded" merely indicates that the scrubbing solution or solutions, after scrubbing the gaseous stream, contain finite quantities of one or more of the impurity gases mentioned.

More particularly, aqueous scrubbing solution containing dissolved HCN, NH₃ and COS, is fed to a stripping zone or stripper where the impurity gases are stripped from the solution. This procedure is accomplished advantageously by forwarding solution from the scrubbing zone as a bleed stream therefrom, to a stripping zone wherein suitable techniques are employed to strip the impurity gases from the solution.

In the stripper, the scrubbing solution may be stripped by heating, contact with a non-reactive gas, or a combination of heating and gas flow stripping. The stripping produces a gas stream containing HCN, NH₃ and COS. The stripped solution, as indicated, may contain solids or fines, these fines being present from infinitesimal amounts to amounts of from about 2% by weight to about 5% by weight. The fines content may determine final treatment or disposal of the solution. The stripped solution can be returned to the scrubbing zone for reuse.

Whatever the case, as indicated, the scrubbing solution may be stripped by heating, or by use of flow of a non-reactive gas (or both). If heat alone is applied to the scrubbing solution, sufficient heat will be supplied to release the dissolved gases. It is not necessary to heat the stripped gases before entry of the gases into the gasification reactor. Suitable devices for this approach include, for example, a conventional packed or tray column with a reboiler. Generally, temperatures on the order of about 100°C to about 300°C, advantageously from about 200°C to about 300°C, will be sufficient to release the dissolved gases.

If a non-reactive stripping gas is employed, it will be supplied at a suitable pressure, for example 3 to 5 atmospheres, to strip the dissolved gases from the scrubbing solution. Any suitable stripping device may be used, such as packed column or a tray column. Different devices may be used (whether stripping is accomplished by heat, gas flow, or a combination thereof) where plugging by solids may be a problem. In any event, any suitable non-reactive gas may be employed. As used herein, the term "non-reactive" implies that the gas does not react with the scrubbing solution to any substantial extent. Suitable gases, under the conditions in the stripping zone, include air, steam, carbon dioxide, oxygen, nitrogen and inert gases. Steam is much preferred, since it can provide heat for the stripping and may be condensed easily, leaving a relatively concentrated stream. Those skilled in the art may adjust volumes and velocities of the stripping gas to appropriate levels. As indicated, heat may be supplied in the case of a stripping gas to assist the stripping.

The stripped impurity gases are separated and removed from the scrubbing solution and forwarded to a gasification reactor. If a multiplicity of gasification reactors is employed in the gasification zone, the impurity gases from the stripping zone may be sent to any one or all of the reactors, as desired or appropriate. If the gasification reactor is operated under high pressure, as is commonly the case, the pressure of the impurity gas stream must be increased for entry of the gases into the reactor. Suitable devices for doing so are within the skill of the art, and as such,

form no part of the present invention.

The invention will now be described in more detail by way of example with reference to the accompanying drawing, in which the figure schematically represents the process of the invention in which auxiliary equipment, such as valves, pumps, etc., have been omitted therefrom. All values are merely exemplary or calculated.

Accordingly, pulverulent coal is passed via a line 10 (1) into a coal dryer (2) where the coal is dried, suitably at a temperature of about 220°C. The dry coal is subsequently discharged through a line (3) and passed into a gasification reactor (4) where it is gasified at a temperature of about 0600°C to about 15 2000°C, a pressure of about 35 atmospheres absolute, with oxygen, which is supplied through a line (5). The gasification produces a product gas which is removed from the upper portion (6) of the reactor, and a slag which is removed from the lower 20 portion of the reactor via a line (7). The gasification product is passed via a conduit (8) through a boiler or heat exchanger (9) where it is cooled to a temperature of about 200°C. In the boiler (9), water which is supplied through a line (10) is converted by indirect 25 heat exchange to high pressure steam, the steam being discharged through a line (11). The cooled gasification product is passed through a line (12) to a device for primary solids removal for example a series of cyclones (13) where the bulk of the particulates 30 (flyash) is removed, and thence to a scrubber (14) where it is contacted with an aqueous scrubbing solution. Water supplied through a line 15a and/or recycle scrubbing water solution are supplied to the scrubber (14) through a line (15). In the scrubber (14), 35 the scrubber solution absorbs HCN, ammonia and COS present in the gaseous stream, and removes soot and remaining ash therefrom. Purified synthesis gas passes from the scrubber (14) through a line (16) on to further treatment and/or recovery. Scrubbing water, containing dissolved gases, and ash and 40 soot, is removed from the lower portion of the scrubber (14) and is sent by a line (17) to an optional filtration zone (18) where the soot and ash particles may be removed. From the filtration zone (18), the 45 scrubbing solution is sent via a line (19) to a stripping zone (20). The stripping zone (20) comprises a stripper contactor of the tray type, in which liquid is introduced into the top of the column and a non-reactive gas is introduced via a line (21) into the 50 bottom of the column. Steam, at a suitable temperature, for example 15°C can be employed in stripping the gases, so that upon leaving the column (20), through a line (22), the now freed impurity gases and the steam in the line (22), are suitably compressed in a compressor (23) and forwarded directly via a line (24) into the gasification reactor (4). The input ports in the gasification reactor may be the ports already present which are used for introduction of other reactants, or they may be ports specially provided for entry of the gas containing the HCN, NH₃ and COS. The ports may be located so as to optimize conversion of the aforementioned materials to substances which can be disposed of easily. Stripped scrubbing solution is returned via the line (15) to the 60 scrubber (14) or may be discharged via the line 15a. 65

While the invention has been illustrated with particular apparatus, those skilled in the art will appreciate that, except where specified, other equivalent or analogous units may be employed. The term

- 70 "zone", as employed in the specification and claims, includes, where suitable, the use of segmented equipment operated in series, or the division of one unit into multiple units to improve efficiency or overcome size constraints, etc. For example, a series of scrubbers might be employed, with different aqueous solutions, at least the bulk of the "loaded" solutions being sent to one or more strippers. Parallel operation of units, is, of course, well within the scope of the invention.
- 75 80 Various modifications of the present invention will become apparent to those skilled in the art from the foregoing description and accompanying drawing. Such modifications are intended to fall within the scope of the amended claims.

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CLAIMS

1. A process for the gasification of carbon-containing fuel comprising the steps of
 - 90 (a) partially combusting particulate carbon-containing fuel in a gasification zone comprising at least one gasification reactor, and producing a gaseous stream containing synthesis gas, particulate matter, and minor amounts of HCN, NH₃ and COS;
 - 95 (b) cooling said gaseous stream, and removing at least the bulk of the particulate matter therefrom, and scrubbing said gaseous stream in a scrubbing zone with an effective amount of an aqueous scrubbing solution and removing HCN, NH₃, COS and remaining particulate matter from said synthesis gas, producing a purified synthesis gas and loaded scrubbing solution;
 - 100 (c) stripping the bulk of the HCN, NH₃ and COS from at least a portion of said loaded scrubbing solution in a stripping zone, producing a gas mixture containing HCN, NH₃ and COS, and a stripped liquid mixture, and removing said gas mixture from said stripped liquid mixture and said stripping zone; and
 - 105 (d) introducing at least a portion of said gas mixture into at least one gasification reactor of said gasification zone.
2. The process as claimed in claim 1 wherein at least the bulk of the stripped liquid mixture is sent to the scrubbing zone for use therein as aqueous scrubbing solution.
- 110 3. The process as claimed in claims 1 or 2 wherein particulate matter is separated from the loaded scrubbing solution prior to entry into the stripping zone.
- 115 4. The process as claimed in claims 1-3 wherein particulate matter is separated from the stripped liquid mixture prior to being introduced into the scrubbing zone.
- 120 5. A process for the gasification of carbon-containing fuel according to claim 1 substantially as hereinbefore described with reference to the accompanying drawings.

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